CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Definition of Dispersion Polymerization

The term dispersion polymerization has been defined as the method for producing polymer particles in the diameter range between suspension (100-1000 μm) and emulsion (0.01-0.1 μm) that is in the range of 10 μm (8). Dispersion particles are formed from an initially homogeneous reaction mixture, by polymerization in the presence of a suitable steric stabilizer polymer. The solvent is selected to be a good solvent for the monomer and steric stabilizer, but a poor solvent for the polymer being formed. Table 2.1 shows the characteristic parameters of dispersion system (9)

Table 2.1 Characteristic parameter of dispersion systems

Diameter μm	Sp surface area, cm2/ml of monomer	No. of particles/ml of monomer	Polymerization technique
0.01	6,000,000	2×10^{18}	emulsion
0.1	600,000	2×10^{15}	
1	60,000	2×10^{12}	dispersion
10	6,000	2×10^{9}	
100	600	2×10^{6}	suspension
1000	60	2×10^{3}	

2.2 General Features of Dispersion Polymerization

In principle, the conditions for a successful dispersion polymerizaton require the presence of an inert diluent which dissolves the monomer and the polymeric dispersant but precipitates the polymer. The polymeric dispersant stabilizes the polymer particles as they are formed by the attachment of a dissolved protective layer around them. Provided these conditions are fulfilled, polymer dispersions may be prepare using any type of polymerization mechanism: free radical, ionic additon,

condensation, ring-opening and so on. The main field of practical application has so far been with free radical dispersion polymerization such as vinyl acetate, vinyl chloride, methyl methacrylate and acrylonitril, in mainly aliphatic hydrocarbon diluents.

A typical dispersion polymerization begins slowly and gradually accelerates a maximum rate somewhere between 20% and 80% conversion followed by a diminution in rate as monomer is consumed. Under normal conditions, conversion above 99% are attained over a period of an hour or so (10).

A number of features can be regarded as characteristic of free radical dispersion polymerization:

i) The insoluble polymer precipitates from an initially homogeneous reaction mixture.

ii) Polymer particles are formed at very early stage of the polymerization. Usually little or no polymerization can be detected before the first appearance of opalescence.

iii) The rate of polymerization steadily increases to a maximum value. The auto-acceleration of polymerization rate is quite distinct from the delayed onset of polymerization during the induction period, which results from inhibition due to impurities. Thorough purification and deoxygenation eliminate the induction period, but leaves the auto-acceleration unchanged.

iv) In many cases, the rate of dispersion polymerization is much faster than the corresponding polymerization in solution using the same quantities of reactants. However, the degree of enhancement in rate depends very much on the nature of the monomer.

Dispersion polymerization therefore, may be regarded as a form of precipitation modified by the presence of a polymeric dispersant to prevent flocculation and aggregation of the precipitated particles. When the process is carried out in the absence of an agent for stabilizing the dispersion, although an opalescent dispersion of polymer particles is formed initially, rapidly flocculates, aggregation continues and polymerization accelerates, sometimes with explosive violence.

Normal suspension polymerization is a reaction in bulk, the monomer is emulsified in water using a surfactant or suspending agent, but the initiator is dissolved within the monomer droplets rather than in the aqueous diluent. The monomer droplets themselves are formed in the aqueous phase.

In emulsion polymerization, the monomer is emulsified in a non-solvent, usually water, in the presence of a surfactant. A water-soluble initiator is used and particles of the polymer form in the aqueous diluent as the reservoir of monomer in the

emulsified droplets is gradually used up. According to Harkins and others (11-12), surfactant micelles are the site of particle formation, although Roe has suggested that they merely serve as a source of surfactant and monomer (13). In both suspension and emulsion polymerizations the rate and degree of polymerization depend on the number of polymerization sites (14).

The similarities and differences between dispersion, emulsion, and suspension polymerization are summarized in Table 2.2 (15).

Table 2.2 Comparison of the Different Types of Particulate Polymerization

	Emulsion	Dispersion	Suspension
Monomer	Droplets Micelles/particles Little in medium	Particles Mostly in medium	Droplets Little in medium
Initiator	Mostly in medium	in Particles and medium	in Particle/droplet
Stabilizer	May be present	Necessary	Necessary
Surfactant	Present	None	None
Initial Homogeneity	Multiple phase	Single phase	Dual phase

There is usually some emulsion formed during suspension polymerization. However, because of the small specific surface area of the suspension particles, it is negligible. In dispersion polymerization, on the other hand, the droplets are small and therefore the effect of the emulsion polymerization can be considerable (14).

2.3 The Scope of Dispersion Polymerization

Dispersion polymerization generally involves the polymerization of a monomer dissolved in an organic diluent to produce insoluble polymer dispersed in the continuous phase in the presence of an amphipatic graft or block copolymer as the dispersant. The copolymer dispersant can either be prepared separately or its precusor can be added to the dispersion polymerization to undergo grafting reactions simultaneously with the growth of polymer. Clearly, dispersion polymerization is quite different from an aqueous emulsion or a suspension polymerization in which the

monomer has only a limited solubility in the aqueous phase and also requires surfactant for its stabilization in the emulsified form.

In dispersion polymerization, any mode of polymerization which produces polymer insoluble in the continuous phase can be used. Free radical addition polymerization has been the most widely applied. Technique of condensation polymerization can also be utilized, using soluble reactants in the usual way. However, in cases in which the reactant are insoluble in the required organic medium, it is possible to use copolymer dispersants which are required for the dispersed polymer produced. The dispersed nature of the reactants often allows the removal of the by-products of the condensation polymerization at a more rapid rate than the corresponding process under bulk conditions.

The organic diluent in dispersion polymerization is normally selected on the basis of suitable boiling point for the type of polymerization and initiation to be used since the dispersion polymerization is usually carried out under reflux conditions.

The kinetic characteristics of free radical addition dispersion polymerization, which enable fast polymerization rates to process within the polymer particles independent of their particle size, and the ready removal of the heat of polymerization produced from the mobile dispersion, is particularly suitable for the development of continuous polymerization techniques. In addition, the degree of control over the size of the polymer particles produced by dispersion polymerization which the appropriate choice of the nature, amount and use of a graft copolymer makes possible, can be exploited to prepare bimodal and polymodal distributions of polymer particles. With the use of the appropriate reactive comonomers in dispersion polymerization, dispersions of reactive polymers may be obtained (16).

2.4 Basis for the Steric Stabilizer

Dispersion stability is normally achieved by the interposition of repulsive forces of sufficient magnitude to overcome the inherent attractive forces of electromagnetic origin which arise as particles approach each another. The steric stabilization is accomplished by the use of repulsive forces generated by the interaction of opposing dissolved polymer chains attached to the dispersed polymer particles. In the absence of any repulsive forces, the particles rapidly aggregate. As two surfaces, each covered by a layer of adsorbed soluble polymer chains, approach each other to within a distance less than the combined thickness of the adsorbed layers, an interaction between the polymer layers will occur. This interaction, which is the

source of steric stabilization, will in most cases, generate a repulsive force between the opposing surfaces and many attempts have been made to describe its nature and magnitude. The problem has usually been treated in terms of the change in free energy which takes place when the two surfaces covered by adsorbed polymer are brought together from an infinite separation to some small, specified distance apart. It must be realized at the outset however, that although a calculation of the free energy change, particularly when restricted to specific regions of polymer perturbation in the liquid phase between the particles, can reserve for the estimation of the magnitude of the interaction, it cannot provide information directly about the actual mechanism of repulsion. Repulsive forces can only be generated between the particles by events occurring immediately adjacent to their surfaces. So far, the theories of steric stabilization have mainly been based on the basic model of an array of polymer chains each attached to a surface by one or at most a few links. The free energy changes accompanying the various interactions of the polymer chains, including interactions with each other, with solvent molecules, with similar chains on as opposing surface and with the opposing surface itself, have already been considered as contributing to the repulsive forces which give rise to steric stabilization (17).

The function of the dispersant (or steric stabilizer, matrix polymer) in a sterically-stabilized dispersion is, therefore, to provide a layer of material solvated by the dispersion medium on each particle surface. Every particle is thus surrounded by a tenuous cloud of freely-moving polymer chains which are, in effect, in solution in the continuous phase. This layer prevents the particles from coming into direct contact and also ensures that at the distance of closest appproach of the two particles, the attraction between them is so small that thermal energy renders contact reversible (16).

The simplest model of a polymer molecule used is that of a freely-jointed chain in which each segment is of equal length but is effectively volumeless. The polymer chains were terminally attached at a plane or spherical surface, so that no desorption or lateral displacement of the chain can occur. The chains are considered to be either so widely spaced on the surface that they can be treated as individual chains to be so close together that the layer can be considered as uniform in composition parallel to the surface. In each case, the chains naturally adopt mean configurations which represent their lowest free energy states. Any constraint on the chains which alters this mean the configuration must therefore increase the free energy of the system. If such constraint arises from the approach of any obstruction from the direction having a component normal to the primary surface, the change in free energy will be manifested as a force of repulsion. this repulsion will act initially only upon those segments of the primary polymer chain which are prevented from occupying a site already filled, but then,

because the whole configuration of the adsorbed chain is modified by this repulsion in the outer region, the concentration of segments at the surface increases, so that the surface itself is subjected to a repulsive force (17).

The nature of the stabilization process can be explained in simple terms in the folloing way. When two particles which have polymer molecules firmly attached to their surfaces approach one another in a medoum in which polymer molecules are soluble, a change in free energy (ΔG_R) occurs as the polymer molecules interpenetrate or are compressed. The resulting increase in the concentration of the polymer segments in the layers of adsorbed polymer generates an osmotic pressure, i.e. ΔG_R is positive. To counteract this effect, solvent diffuses into the regions of higher polymer concentration forcing the particles apart until the steric barriers are no longer in contact. An effective stabilizer must therefore be able to maintain a complete coverage of the particle surface. In addition, the solvated cloud surrounfing the particles must be a thermodynamically good solvent for the stabilizing polymer chains and also concentrated enough to generate sufficient osmotic pressure to resist the inherent attractive forces (18).

2.5 Theoretical Model of Dispersion Polymerization

The following model has been used as the basis for interpreting the experimental results which follow.

At the start of the process of dispersion polymerization, monomer, stabilizer and initiator are in homogeneous solution in the diluent. Initially, polymer molecules formed by solution polymerization aggregate in small group with stabilizer molecules to form stabilized particle nuclei, probably less than 0.01μm in diameter. This stage is completed very rapidly (well under 1% conversion). For the kinetic analysis, it is assumed that particles are present from the start. The number of particle nuclei increased (and particle size decreases) with increasing stabilizer content, but very few new particles are formed after the first crop, unless a substantial further amount of stabilizer is added (19).

Once polymer particles have been formed from the initially homogeneous reaction mixture, they absorb monomer from the diluent phase and polymerization subsequently proceeds within the particles. Polymerization takes place according to the laws of bulk polymerization kinetics. In the condition used here, the high viscosity of this monomer-swollen polymer phase greatly hinders radical termination. The resulting increase in radical concentration due to the gel effect accelerates the rate of polymerization (Trommsdorff effect (20)), while the slow rate of termination also

ensures that many radicals can coexist in each particle, in contrast to the situation which envisages in classical emulsion polymerization kinetics.

Any radicals initiated in the diluent phase are swept up by particles before they have had time to grow to more than a very few monomer units in length. Consequently, initiation can be considered as taking place as though all the initiator were confined within the particles, even though the types of initiator used are known to be distributed between the polymer particle and diluent. This results in an enormous decrease in the effective radical concentration in the diluent phase, suppressing both solution polymerization and the formation of new particles. Since all radicals formed rapidly find their way to the particles, this implies that we can treat the initiator from the kinetic point of view as if it were all in the particle phase, even thought in fact the typical initiators used are partitioned between particles and diluent.

A kinetic equation corresponding to this model for dispersion polymerization has been developed in the following manner. If the polymer particles at a given time occupy a volume fraction v of the whole dispersion, and the rate of initiation in the whole dispersion is R_i, then the effective initiation rate in the particle will be given by

$$R_i' = R_i/v \tag{2.1}$$

If the monomer concentration in the particles is C_p, the overall polymerization rate in the particles, R_p', will be equivalent to the usual expression for bulk or solution kinetics in the form

$$R_p' = C_p k_p (R_i'/k_t)^{1/2} = C_p k_p (R_i/v k_t)^{1/2} \tag{2.2}$$

Here k_p is the propagation rate constant and k_t is the termination rate constant (define with respect to rate of disappearance of single radicals, not pairs (23)).

Since this take place in the volume fraction v, the overall rate of polymerization in the whole dispersion is

$$R_p = v R_p' = C_p k_p (v R_i/k_t)^{1/2} \tag{2.3}$$

This is the basic equation for dispersion polymerization of the model proposed here. Since the rate is based on bulk polymerization kinetics, it is in principle independent of particle size and number, proviced that it is not limited by rate of diffusion of monomer into the particles.

In emulsion polymerization, the monomer concentration in the particles is generally taken to be in equilibrium with a saturated aqueous solution throughout much of the course of polymerization and is only limited by the center effects of interfacial tension in the very small droplets (21). Thus the concentration of monomer on the particles is usually taken as constant up to the point where free monomer droplets disappear. In dispersion polymerization, the situation is very different because monomer is completely miscible with diluent and the monomer concentration in the particles is subject to a conventional partition equilibrium, which greatly outweights any effects of interfacial tension. The concentration of monomer in the polymer particles depends on its partition coefficient, α, between polymer and diluent. Here a first approximation can be represented by a simple partition coefficient, α which may be taken as constant (but may in fact vary slightly with monomer concentration). Then, an approximated expression for the overall rate of polymerization, where C_m is the overall monomer concentration in the dispersion (it should strictly be the monomer concentration in the diluent), is given by

$$R_p = \alpha C_m k_p (vR_i/k_t)^{1/2} \tag{2.4}$$

This is the general equation for the dispersion polymerization and it takes into acount the principal features of the kinetics which have been established, such as the proportionality of the polymerization rate to the square root of initiator concentration, the acceleration in rate which follows the increase in the total volum of polymer particles and the correlation of rate with that in the bulk polymerization of the monomer. It is important to note that the value of $k_p/k_t^{1/2}$ in this expression is not to be taken as constant but varies as the concentration of the monomer in the polymer particles changes, in exactly the same manner as in bulk polymerization at high conversion. In principle, the partition coefficient may also vary with monomer concentration, but the variation is usually not great and a constant value is a sufficiently good approximation for use in most of the kinetic experiments.

The kinetic model proposed differs from the conventional treatment of emulsion polymerization in that there is no enhancement of rate due to the isolation of radicals in separate particles (22). In dispersion polymerization, factors such as the size of the polymer particles formed, their relatively low absorption of monomer and consequent high internal viscosity and the high rates of initiation used, all contribute to a retardation of cross-termination of radicals within the particles to allow many radicals to coexist in each particle over the whole extent of the polymerization.

2.6 Theories of Particle Formation

There is as yet no single definitive theory able to predict quantitatively the number of particles formed in a dispersion polymerization under defined conditions. It is worthwhile bearing in mind that this is still also the situation in the field of aqueous emulsion polymerization. Here, some approaches which can contribute to a theoretical treatment of particle formation are examined (23).

2.6.1 Equilibrium System and Irreversible Processes

Some systems are known in which a phase separates out in the form of particles or domains of well-defined size and number according to a true thermodynamic equilibrium. In all of the equilibrium systems, growth beyond a certain size is limited because it would force parts of the added molecules into energetically unfavorable situations, and equilibration is possible only because the mobility or solubility of the separating phase is high enough to permit it. In contrast to such equilibrium systems, the formation of particles in dispersion polymerization must clearly be regarded as an irreversible process: once formed, the particles are thermodynamically stable and continue to grow. Moreover, further polymerization within the particles lowers their solubility to a point where transfer of material from one particle to another is virtually impossible. The number and sizes of particles are therefore determined by the balance of several competing rate processes and the way they vary during the course of polymerization. The most importance of these is the rate of nucleation, i.e. the rate of formation of new particle nuclei and the way in which this is related to the number and size of existing particles, the presence of a dispersant and the rate at which new polymer chains are initiated in the diluent phase.

2.6.2 Qualitative Models of the Nucleation Process

The nucleation process starts in an essentially homogeneous solution containing monomer, initiator and usually an amphipathic dispersant. Exactly as in conventional solution polymerization, the first steps involve production of radicals by breakdown of the initiator, which in turn reacts with monomer to form growing oligomeric chains with a reactive free redical at the end.

Three different models have been proposed for the formation of particle nuclei from these growing oligomer chains (Figure 2.1):
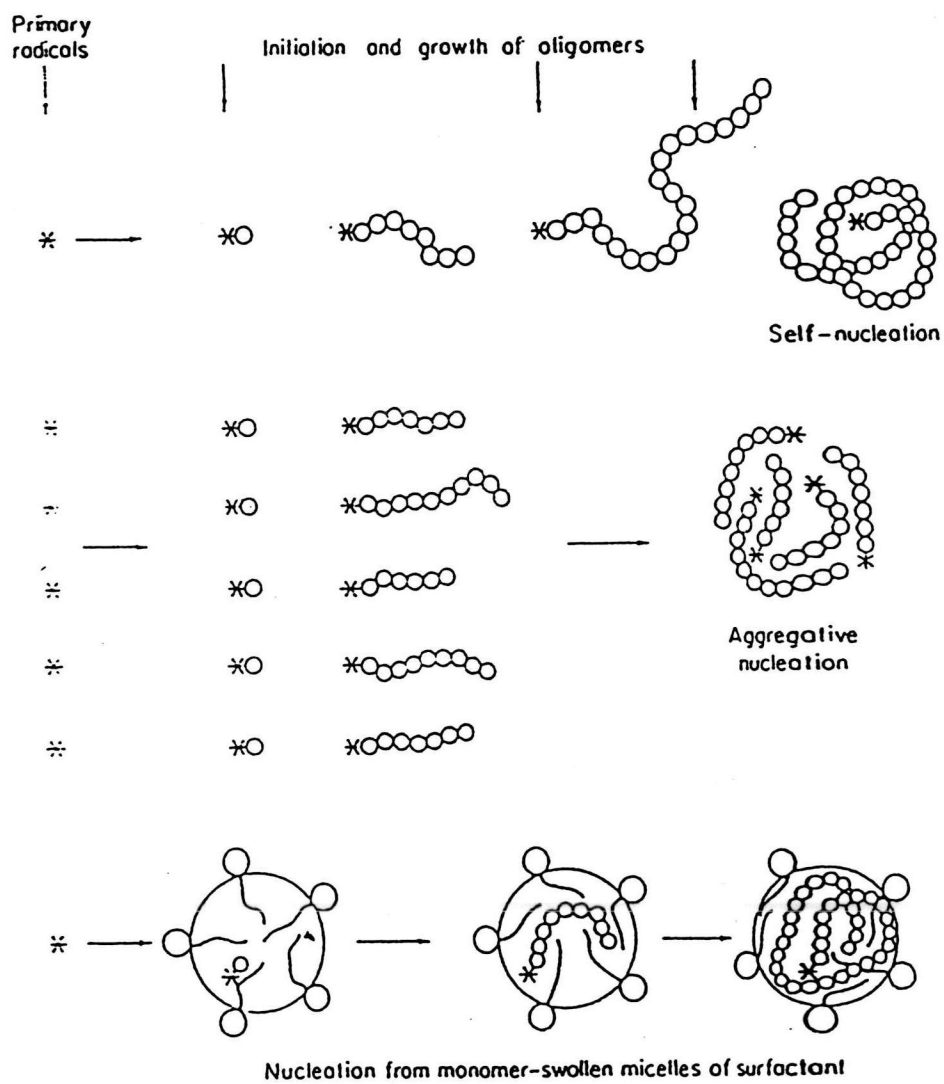
Figure 2.1 Three models for the formation of nuclei

2.6.2.1 <u>Self-nucleation</u>: Each individual oligomer chain as it grows, at first has as extended configuration in solution, but then collapses into a condensed state when it reaches a certain threshold molecular weight depending on its solubility in the medium. These oligomers are produced throughout most of the reaction, and as a result, they differ in length and molecular weight. This is primarily due to the fact that the solvency of the continuous medium changes substantially as the polymerization proceeds and as the monomer is required for precipitation of oligomers is also reduced. Therefore, the nuclei produced differ in size and molecular weight producing a polydisperse particle population. The condensed oligomeric chain therefore constitutes a new particle nucleus. The behavior of each oligomer chain is unaffected by the presence of other oligomer molecules, so every chain initiated forms a new particle unless it is captured by diffusion to an existing particle before it reaches the threshold molecular weight.

2.6.2.2 <u>Aggregative nucleation</u>: Growing oligomer chains associate with each other increasingly as their molecular weight and concentration rise, at first reversibly. The oligomers grow to a critical size and molecular weight in the continuous phase before precipitation out. This increase in the size and number of oligomers causes the oligomers to increasingly interact with each other thus forming aggregates. These aggregates are stabilized against further aggregation by adsorbed stabilized. The important difference between this process and self nucleation processes is that the nuclei are formed almost at the same time resolution in a narrower particle size distribution. The aggregative nucleation mechanism fits the picture of dispersion polymerization in organic media most closely. Aggregates below a certain critical size are unstable, but above this critical size they are stable and tend to grow, constituting new particle nuclei. The rate of nucleation is dependent on the activation energy required to form a critical aggregate, which can in principle be calculated from the interfacial tension between the two phases and the relative supersaturation of the solute. Both rising concentration and rising molecular weight of the oligomer chains therefore result in a sharply increasing rate of nucleation, but capture by existing particles competes with the process of aggregation to form nuclei.

2.6.2.3 <u>Nucleation from micelles</u>: Particle nuclei are formed by growth of oligomer chains initiated in monomers solubilized in micelles of surfactant or amphipathic dispersant. In this process monomer-swollen micelles are considered to be the primary loci for nucleation reaction.

Nucleation processes are influenced by many reaction parameters including the solvency of the continuous medium, temperature, monomer, initiator and stabilizer concentrations, shear and cool rate. However, it is important to note here that, there is no true nucleation process, since the emulsified droplets of monomer are transformed directly into particles. The process is therefore essentially a form of suspension polymerization, and as in the familiar aqueous systems of this type, the size of droplets and therefore the size and number of polymer particles are determined by the amount and nature of the amphipathic emulsifier, the viscosities of the two phases and the degree of agitation used in the emulsification stage.

2.6.3 Suppression of Nucleation: Capture of Oligomers

If no competing process came into action, the formation of particle nuclei might be expected to continue throughout the course of polymerization as long as free monomer remains. In the aggregation model, the build-up of oligomers above the supersaturation threshold would result in an initial brust of nucleation followed by a fall as supersaturation is lowered due to precipitation of particles, reaching a steady-state level in which the rate of initiation of the oligomers is balanced by their rate of loss to form nuclei. Alternatively, according to the self-nucleation model, the rate of nuclation would follow the rate of initiation throughout, falling gradually as monomer becomes depleted.

In practice, of course, the rate of formation of particles usually falls to a negligible level very early in the course of polymerization, unless conditions are substantially altered: once many particles are present, the formation of new particles is strongly inhibited. The most likely reason is that nearly all the oligomer molecules forming in the diluent phase are captured by existing particles before they can form new nuclei. Indeed they are probably captured while still very small and continue to grow within the particles, serving essentially as a source of radicals from the diluent.

2.6.4 Particle Formation in the Presence of Dispersants

The nature and amount of dispersant used in a dispersion polymerization has a profound effect on the occurrence of nucleation and the numbers of particles formed as well as preventing flocculation. It is possible to propose a plausible role for the dispersant molecules in modifying each of the processes postulated in the various

theoretical models, and a great deal of further work is needed to establish exactly the complete role which a dispersant plays in any given polymerization system. In each case, enhanced nucleation is accounted for by some form of association between the dispersant and the growing oligomer which raises the probability of forming a nucleus and in turn, lowers the probability of capture by existing particles. The effects of increasing polarity and insolubility of both the anchoring portion of the dispersant and the polymer being formed therefore fall naturally into place since these will increase the tendency to associate and hence increase the rate of nucleation (Figure 2.2)

So far, it has been tacitly assumed that nucleation is brought to halt by prior capture of oligomers while there is still excess unused dispersant present, so that the concentration of dispersant can be taden as ruoghly constant throughout the nucleation period. However, there are two possible situations in which depletion of dispersannt could become the limiting factor determining particle size and number:

2.6.4.1 <u>Dispersant- limited nucleation</u>: The dispersant is so efficient that nucleation continues at a high rate until there is very little dispersant remaining unattached to particles; thereafter nearly all oligomers are captured by particles. This behaviour has been taken as the normal situation in emulsion polymerization, there is little evidence for its widespread occurrence in organic media, at any rate in such an extreme form.

2.6.4.2 <u>Dispersant-limited agglomeration</u>: Primary particles grow in size and in number until the dispersant available is insufficient to cover the surface effectively and prevent flocculation. In principle, this may occur either while nucleation is still under way, or well after it has been brought to a halt by prior capture of oligomers. The usual practical result of running out of dispersant in a dispersion polymerization is gross flocculation throughout the dispersion, but in certain circumstances controlled agglomeration occurs instead, to form fewer and larger particles with a smaller total surface. In its extreme form, this model assumes that the dispersant serves merely to prevent secondary aggregation and plays no part in the formation of primary particles.

2.6.5 Present Status of Theories of Particle Formation

The theory most widely applied to emulsion polymerization-nucleation continuing until insufficient dispersant remains to saturate the growing particle. The
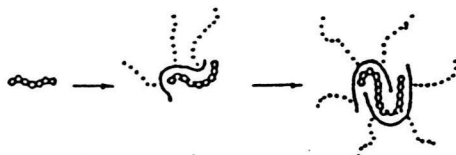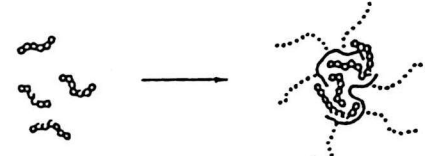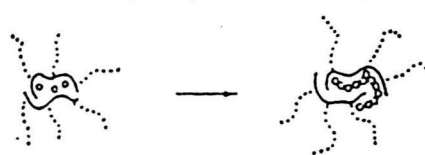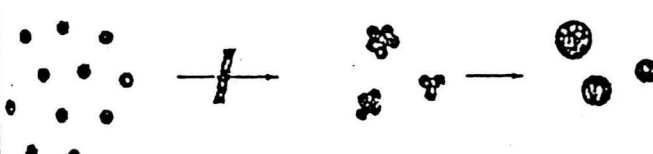
SELF – NUCLEATION	Dispersant stabilizes growing oligomers against capture by particles at lower molecular weights ∴ Reduces probability of capture ∴ Produces more nuclei
AGGREGATIVE NUCLEATION	Dispersant participates in forming incipient nuclei and reduces interfacial tension ∴ Lowers activation energy and threshold molecular weight ∴ Reduces probability of capture ∴ Produces more nuclei
MICELLAR NUCLEATION (probably only in aqueous systems)	Dispersant forms micelles from which nuclei are formed by initiation of monomer solubilized in them. Dispersant migrates from micelles to cover particle surface ∴ Nucleation stops when no micelles remain, so is limited by amount of dispersant
AGGLOMERATION	Dispersant prevents or limits agglomeration of small particles to form larger ones ∴ Total particle surface area and hence number of particles, is limited by amount of dispersant

Figure 2.2   Probable roles of dispersant in modifying particle formation process

evidence indicates that nucleation is normally completed while excess dispersant is still present and supports the view that capture of growing oligomers by particles is the main factor suppressing nucleation. Dispersant therefore merely modifies a process which is already operative in unstabilized precipitation polymerization. On the other hand, the amount of dispersant available can become the limiting factor at a later stage of particle growth, resulting in secondary agglomeration under certain special circumstances, although gross flocculation is the usual consequence.

Application of the classical theory of homogeneous nucleation to dispersion polymerization is so far untested in a quantitative sense, but leads to broadly correct conclusions on the effects of solvency and dispersants, when combined with any of the theoretical treatments of the capture of oligomers by particles. It has provided a semi-quantitative basis for a number of important conclusions:

i) Nuclei probably form by a process of aggregation of oligomers, rather than self-nucleation, since the threshold degree of polymerization for the former may often be quite low (~10-15): a longer chain would be needed to coil enough to form a condensed phase.

ii) The probability of participating in a nucleus rises so steeply with molecular weight, that a single threshold degree of polymerization ,P, above which all oligomers form nuclei is a reasonable approximation in most cases. The number of particles rises as P falls.

iii) P increases with the solubility of the polymer and falls with rising dispersant concentration (falling interfacial tension), but probably changes only slightly during the course of a typical polymerization.

iv) The number of oligomers in a nucleus, Q, may vary considerably with conditions, rising with increasing dispersant concentration; it probaly changes only slightly during the course of a typical polymerization.

v) P is usually sufficiently low so that nearly all oligomers form nuclei (or are captured by particles) before their radicals are terminated. In this case, nearly complete polymerization takes place within the particles, the concentration of polymer in the diluent phase remains extremely low, and nearly all radicals pass into the particle.

vi) Some case may exist where the solublity is marginal: as the degree of polymerization rises, the solubility falls gradually and the probability of capture by particles rises only slowly. P may then be so high that nearly all oligomer radicals are terminated before nucleation or capture; complete polymerization takes place in the diluent phase, where an appreciable concentration of polymer may remain in solution;

particles grow only slowly since few racicals reach them, and nucleation may continue unabated until a late stage in the polymerization. The balance would tend to shift further in this direction as the initiation rate is raised, enhancing the probability of termination in the diluent phase.

On the theoretical side, it must be recognized that the application of bulk properties (free energy of dilution, solubility, interfacial tension) to assemblages of a few molecules is of doutful validity, although it has worked surprisingly well in other contexts, and there is considerable uncertainty about the value of the pre-exponential factor in the rate equation.

2.7 Controlling Factors of the Particle Number and Size

2.7.1 Period of Particle Formation

In a typical dispersion polymerization producing polymer which is very soluble in the diluent, the stage of particle formation is normally completed very quickly. All the evidence from electron micrographs indicates that very few particles form after this stage, therefore, the number of particles remains usually unchanged throughout the remaining course of the polymerization. Those conditions which extend the particle-formation stage over a longer period of time, usually also slow down the rate of particle formaton to a greater extent, so that relatively fewer and larger particles are obtained. This is a normal result of increasing the solvency of the diluent for the polymer (10).

2.7.2 Solvency of the Medium and Solubility of the Polymer

The processes of particle formation are strongly influenced by increasing the solvency of the medium for the polymer which is being produced: i) the onset of particle formation is often retarded, ii) the duration of particle formation is prolonged, iii) fewer particles are produced, and iv) they are correspondingly larger and usually of wider particle size distribution.

For a given polymer, solvency may be varied by an appropriate choice of diluent, addition of strong solvents, or by altering the concentration of the monomer. In most polymer-diluent systems, the effects of changes in temperatre are small conpared with the results of even minor changes in composition but solvency

generally increases with rising temperature. The solvency of the medium of course depends as much on the nature of the polymer as on the nature of the diluent. The insolubility of polymers in aliphatic hydrocarbon diluents runs closely parallel to their polar character and the value of their solubility parameter. In fact, it is very difficult to prepare stable dispersion of polymers with high proportions of monomers at either of the extreme ends of the hierarchy by dispersion polymerization in aliphatic hydrocarbons. On the one hand, excessive amounts of dispersant are needed to stabilize the large total surface area produced, then ultra-fine particles are formed. On the other hand, the less polar polymers are too near complete solubility and their large particles readily aggregate because the dispersant is only weakly anchored to their surfaces. With more polar monomers, these difficulties can be overcome to some extent by using a correspondingly polar diluent such as an aromatic hydrocarbon or an ester. There is an important additional effect of solvent in modifying the orientation of the dispersant and its influence on the number of particles formed. Higher solvency for the polymer moiety which anchors the dispersant to the polymer particles probably reduces the tedency of the stabilizer to associate with growing polymer chains during the process of particle formation, as well as impairing the efficiency of anchoring to the particles which have been formed. Whatever the molecular mechanism, the practical outcome is fewer and larger particles. This is clearly shown by the effect of changing the solubility of the anchor polymer of the dispersant without altering monomer or medium.

2.7.3   Concentration and Nature of the Dispersant

The concentration of the dispersant is one of the most important factors controlling nucleation: the number of particles increases and their size decreases as the stabilizer content is raised. In any given system, the exact relationship must be established empirically. The dependence on dispersant content is very marked up to a certain level, beyond which further additions have much less effect. In very high levels of the dispersion chain solvency, the efficiency of stabilization is seriously impaired and it is possible that secondary aggregation of primary particles occurs under these conditions, so that the final particle size is not very sensitive to dispersant concentration. At low levels of dispersant, the particles have a much wider size distribution with a higher average size.

When the initial concentration of monomer in a dispersion polymerization is very high, the particle size (of course, much larger) is somewhat less sensitive to changes in dispersion concentration.

2.7.4   Reactivity of Dispersant Precursors

Whatever the type of dispersant used, a broadly similar relationship is found between its concentration and the particle size of the dispersion formed: samples have been drawn from both preformed comb-type grafts and precusor-type dispersants. However, in the precusor-type dispersant the true dispersant is formed only gradually from the precusor during polymerization, so that its effective concentration at the critical period when particles are forming depends on the relative rates of this grafting reaction and the polymerization of the monomer. For this reason, the particle size falls as the proportion of reactive groups in the precusor is raised, or if the type of reactive group is replaced by one with reactivity ratios more favourable to copolymerization.

2.7.5   Renucleation, Agglomeration and Flocculation

Renucleation is the formation of fresh particles at a later stage in the polymerization. It is most likely to occur in feed processes, in which the original seed particles grow by further addition of monomer together with more dispersant. Renucleation is inhibited by the presence of existing particles, and in this respect the total number of particles seems to be more important than the total polymer concentration. The effect of renucleation, of course, is to produce a bimodal or polymodal particle size distribution, whilst at the same time preventing the original particles from growing to as large a size as if renucleation had not taken place.

The aggregation of polymer particles occurs in the absence of sufficient effective dispersant to protect the total particle surface, and can take the form of flocculation or agglomeration.

Agglomeration is the formation of new larger particles by the aggregation of limited numbers of primary particles, which may be followed by partial or complete fusion.

Flocculation is the formation of loose aggregates of flocs over extended regions, sometimes throughout the whole of a dispersion, which may then appear to gel or coagulate.

Agglomeration of primary particles can, in principle, afford a means of increasing the size of particles in a dispersion and reducing their number. Such controlled secondary aggregation has rarely been demonstrated conclusively in practice. It would not be expected to be revealed in the shape of the particles formed

since agglomeration would usually be followed by complete coalescence in the conditions normally used in dispersion polymerization. It is therefore necessary to demonstrate that the particle size after aggregation has increased by an amount more than could be accounted for from the particle size before aggregation and the extra amount of monomer polymerized, or in other words, that the number of particles has decreased.

In principle, it should expect that the agglomeration was favoured by the use of amounts of dispersant which are inadequate to provide complete stabilization. However, the use of inadequate amounts of the dispersant usually results in gross flocculation and coagulation of the dispersion, rather than in agglomeration. In fact, one of the most important aspects in developing practical formulation, is the establishment of practicle limits to the amount and rate of addition of dispersant sufficient to prevent flocculation, but small enough to avoid too much renucleation. Paradoxically, excessive renucleation can also lead to subsequent flocculation because the additional dispersant cannot keep pace with the extrasurface formed by growth of the new particles. It is conceivable that agglomeration processes may occur after primary particle formation in the more typical conditions of dispersion polymerization in aliphatic hydrocarbons. However, the weight of evidence from electron micrographs point to constancy of particle numbers from a very early stage and if any such agglomeration takes place it must be almost immediately after the primary nucleation stage, or even concurrent with it.

In addition, random agglomeration would be expected to give a wide range of particle sizes whereas a fairly uniform particle size is usually observed in dispersion polymerization unless the solvency of the medium is very high or changes substantially, or more dispersant is added. In practice also, the number of particles ususlly appears to be essentially contant from a very early stage, if insufficient dispersant is present to stabilize the increasing surface area, the latex undergoes a fairly sudden and gross overall flocculation rather than a more gradual coalescence to form larger particles. Presumably, an essential requirement for controlled agglomeration rather than overall flocculation is that the dispersant is able to redistribute itself rapidly from the surface lost by agglomeration to protect the remaining surface before further agglomeration ensues.

2.8 Literature Review

There has been substantial interest in monodisperse micron size polymer particles ever since J.W.Vanderhoff and E.B.Bradford announced their preparation of

polystyrene particles with highly uniform particle size in 1955 (24). Monodisperse particles are finding a wide variety of applications including instrument calibration standards, standards for the determination of pore size and the efficiency of filters, column packing material for chromatographic separation, support materials for biochemicals, and so on (15).

Control of particle size and its uniformity has been a major area of interest; it proves to be particularly challenging to prepare monodisperse polymer particles in the micron size range (2-20μm). Traditionally the attempt to prepare micron-size particles has been to break up monomer droplets into the micron size range by homogenization in the presence of a stabilizer, and subsequently polymerize the monomer by a suspension polymerization (8). This proves to be an inefficient method of achieving monodispersity because of the inherent size distribution in the mechanical homogenization step.

The early work on the kinetics of dispersion polymerization with particle sizes usually in the sub-micron range suggested that once the particle nuclei have formed they absorb monomer and sweep up most of radicals in the continuous phase (19). The gel effect was found to be very significant. Molecular weights of the final polymers were on the order of 10^6. The more study (15) showed that the rate of dispersion polymerization was slow, and molecular weight of the final polymers was on the order of 10^4 when more polar dispersion media were employed. The mechanism was entirely one of solution polymerization, since no gel effect was observed. Monodisperse latex particles in the size range of 3-9 μm were produced. It is believed that the partitioning of monomer and initiator between the polymer and continuous phases plays an important role in altering the polymerization process in this systems (25).

Latexes with relatively narrow particle size distributions (coefficient of variation <2%) have been prepared by seeded emulsion polymerization to latexes of smaller particle size, either by Vanderhoff's successive seeding method (33) or Ugelstad's two-stage swelling method (1). The preparation of monodisperse latex particles by dispersion polymerization in organic media (15, 27, 28) has recently received great attention because of the simplicity of the process and the wide variety of monomers which can be polymerized into polymer particles by this process.

Monodisperse micron size polymer particles could not be prepared in reasonable quantities until Ugelstad et al. developed a method of growing sub-micron particles using a two-step swelling technique (1). In this method, submicron polymer seed particles are made by surfactant-free emulsion polymerization. The seed particles are subsequently suspended in a new medium and then swollen with monomer and oil-

soluble initiator by the addition of an emulsion of low molecular weight compound which diffuses from the emulsion droplets into the polymer particles. This small molecule is insoluble in water and does not normally diffuse through the water, so a low boiling point water soluble aprotic solvent is used to facilitate the transport. The presence of small molecules soluble in the polymer particle dramatically increases the amount of monomer which can be incorporated in the seed particles. The addition of the aprotic solvent permits the otherwise insoluble compound to diffuse and upon removal of the aprotic solvent, the small molecule is locked into the particle. Owing to the entropic dilution effect, this small molecule allows further swelling of the particle by monomer which, upon subsequent polymerization, gives rise to micron-size particles as large as 50 μm. This technique provides a very elegant route to micron- size particles but it is very tedious and difficult to carry out. There is sufficient interest in such particles that Vanderhoff and co-workers have been contemplating the growth of polymer particles to the micron size range aboard the space shuttle in microgravity (2).

A second approach to prepare the micron size particles is by dispersion polymerization. This method has been very thoroughly reviewed by Barrett (29). Barrett's experiments were conducted primarily in organic media and particles up to 1 μm in size and it has been shown to produce particles with a very narrow size distribution. The process differs considerably from emulsion polymerization in that only a single phase is present at the beginning of the polymerization. After initiation the polymers grow in solution to a critical size at which point nucleation takes place. Growth of the nuclei then proceeds to give the final particles. The process involves the polymerization of a monomer dissolved in a medium in the presence of a graft copolymer dispersant (or its precursor) to produce in soluble polymer dispersed in the medium. The graft copolymer functions as a steric stabilizer, which can prevent flocculation and aggregation of the particles being formed. Since this method depends on incipient aggregation of the polymerizing species at the early stages of the polymerization, the numbers of particles are determined by these growing nuclei. The final size and distribution are largely determined by the amount of monomer introduced and the ability of the stabilizer to maintain the colloidal stability of the growing particles. Using a variation of this approach, M. Levy et, al. have successfully prepared monodisperse polymer particles in the range of 1-6 μm (28). Their method involves the use of a polymeric steric stabilizer in combination with a quaternary ammonium salt which the authors claimed that it acts as an electrostatic co-stabilizer.

Recently, C. K. Ober (30) reported that the solvency or polarity of the dispersion polymerization medium can determine the ultimate size of the resulting polymer particles. Indeed, by using solvents of difference polarity, it was possible to

adjust the average particle size provided all other variables were fixed (though it was noted that changes in the solvent medium usually led to polydispersity). Dispersion polymerization of styrene was investigated in various solvent systems including mixtures of 2-methoxyethanol/ethanol, 2-ethoxyethanol/ethanol, dimethoxyethane/ethanol and tetrahydrofuran/ethanol. Only the first of these solvent systems was found to produce particles with a narrow size distribution, although all systems were capable of producing particles that had particle diameters greater than 10 μm. More recently, it has shown that several other factors are extremely important in determining both the size and size distribution of particles formed by dispersion polymerization (31). These include the temperature of the reaction and the concentration of the initiator. The temperature can affect both the rate of free radical formation and the thermodynamic properties of the polymerization system. However, it was observed that a narrow size distribution could be achieved over a considerable range of temperature provided that a particular concentration of initiator was used at each given temperature. It was also observed that at a particular temperature, larger concentrations of initiator actually produced larger particles. Interestingly, the concentration of initiator was not found to significantly change the overall rate of the polymerization.

Relationships between initiator concentration, reaction temperature, particle size and molecular weight were not observed in Barrett's early studies (19), i.e. the polymerizations of methacrylate, acrylate and vinyl monomers in hydrocarbon media. In general, the particles produced in those systems were sub-micrometer in size and large gel effects were observed which resulted in molecular weights in excess of 100,000. Indeed, Barrett was obliged to add chain transfer agents to his systems in order to control the rapid rise in molecular weight brought on by the gel effect. The polymerization is thus analogous to a suspension polymerization and to the polymerization of the swollen seed particles described by Ugelstad. Ober and Lock (30) reported a similar gel effect when polystyrene particles were prepared by dispersion polymerization in ethanol-water mixtures, it appeared that when monodisperse particle were prepared in methyl cellosolve-ethanol that the final polymer was of relatively low molecular weight and that the mechanism was not related to a suspension polymerization. In other words, partitioning of the monomer into the growing nucleus was not great and incidental to the mechanism.

There are some of the other early works on the non-aqueous dispersion polymerization (32) involved the use of a comb polymer, Stejskal and co-workers (5) have used poly(styrene-b-(ethylene-co-propylene)) to stabilize the dispersion polymerization of methyl methacrylate in decane, obtaining stable particles up to 200 nm in diameter. SEM micrographs of the poly(methyl methacrylate) particles revealed

that under different polymerization conditions the particles were not uniform in size distribution and at least, in one case a bimodal distribution was observed. More recent work in aqueous and alcoholic media (15, 25, 30) has used graftable homopolymers such as hydroxypropyl cellulose and poly(vinyl pyrrolidone) as the polymeric stabilizer. Lok and Ober (15) investigated the dispersion polymerization of styrene in a range of alcoholic media and found that large (1-2 μm), monodisperse particles were formed when hydroxypropyl cellulose was used as the polymeric stabilizer. Where homopolymers are used as polymeric stabilizers, stabilization is thought to involve grafting of monomer to the homopolymer to form the anchor block.

Block copolymers have also been used to stabilize emulsion polymerizations. Recently, Piirma and coworkers (33) reported the use of poly(styrene-b-ethylene oxide) copolymers of low molecular weight as stabilizers in the emulsion polymerization of styrene. Monodisperse particles ca 80 nm in diameter were obtained. Riess and coworkers (32) have also synthesized poly(styrene-b-ethylene oxide) diblock and triblock copolymers compositions and have used these as stabilizers for emulsion polymerizations of styrene and other monomers.

Using electron microscopy, Khan et al. (34) examined dried samples of poly(styrene-b-ethylene oxide) micelles formed in water. They observed two size distribution for the particles; the smaller particles were considered to be micelles, while the presence of the larger particles was attributed to incomplete dissolution/equilibration.